PFWM-3

SAND80-2051C

CONF-801037--13

MECHANICAL PROPERTIES OF CHEMICAL VAPOR DEPOSITED COATINGS FOR FUSION REACTOR APPLICATION*

A. W. Mullendore, J. B. Whitley,
H. O. Pierson and D. M. Mattox
Sandia National Laboratories**
Albuquerque, New Mexico 87185

ABSTRACT

Chemical vapor deposited coatings of TiB_2, TiC and boron on graphite substrates are being developed for application as limiter materials in magnetic confinement fusion reactors. In this application severe thermal shock conditions exist and to do effective thermo-mechanical modelling of the material response it is necessary to acquire elastic moduli, fracture strength and strain to fracture data for the coatings. Four point flexure tests have been conducted from room temperature to 2000°C on TiB_2 and boron coated graphite with coatings in tension and compression and the mechanical properties extracted from the load-deflection data. In addition, stress relaxation tests from 500 to 1150°C were performed on TiB_2 and TiC coated graphite beams to assess the low levels of plastic deformation which occur in these coatings. Significant differences have been observed between the effective mechanical properties of the coatings and literature values of the bulk properties.

*This work is supported by the Office of Fusion Energy, U.S. Department of Energy (DOE), under Contract Number DE-AC04-76-DP00789.

**A U.S. DOE facility.

REA

DISCLAIMER

SAND80-2051C

MECHANICAL PROPERTIES OF CHEMICAL VAPOR DEPOSITED COATINGS FOR FUSION REACTOR APPLICATION*

A. W. Mullendore, J. B. Whitley,
H. O. Pierson and D. M. Mattox
Sandia National Laboratories**
Albuquerque, New Mexico 87185

INTRODUCTION

In magnetic confinement fusion reactors, the interaction of the plasma with limiter surfaces can strongly affect the energy balance of the plasma. Erosion products from limiters can poison the plasma, i.e. cause energy drain via radiation which may prevent the attainment of temperatures sufficient for ignition. One approach to this problem is to coat these surfaces with refractory, low-Z materials such that the combination of erosion rate and atomic number of erosion products is sufficiently low to minimize the losses. The development of coatings which meet this requirement must at the same time deal with the severe thermal shock requirements imposed by the pulsed mode of operation of the tokamak. Even more devastating can be the thermal shock conditions associated with plasma disruption.

*This work is supported by the Office of Fusion Energy, U.S. Department of Energy (DOE), under Contract Number DE-AC04-76-DP00789.

**A U.S. DOE facility.

A program of materials development, characterization and testing at this laboratory has investigated a variety of coated materials for application as limiters. Among these, three prime candidates have been chemical vapor deposited (CVD) TiC, TiB_2 and B on graphite substrates. The various aspects of this program have been summarized elsewhere[1-5] and it shall be the purpose of this paper to discuss recent mechanical property results which relate to the thermal shock resistance of the coatings.

EXPERIMENTAL

In order to perform thermal-mechanical modelling for coated substrates one is usually forced to use bulk mechanical property data for the coating material. This is often a poor approximation, particularly when the coating material is anisotropic or has structural characteristics very different from the bulk material. In this program, the greatest need for the determination of mechanical properties were TiB_2, because of preferred orientation and mechanical anisotropy, and boron, due to the lack of good mechanical property data, even for the bulk form.

The determination of the stress-strain characteristics of thin (10-30 μm) coatings is difficult and subject to variations due to coating thickness non-uniformity, grain structure, defect structure, interface nature, etc. Thus it was necessary to use a test specimen and stress application method which best duplicated the material in its intended application. A four-point bend test of a flat beam of Poco AXF-5Q graphite coated on one side with the TiB_2 or B was chosen. By comparing the load-deflection data (of

coatings in both tension and compression) with similar data from uncoated bars, the stress-strain data for the coating material was extracted. Pretest calculations[6] of the stress-strain characteristics of TiB_2 on Poco graphite lead to a choice of substrate and coating thicknesses such that the expected compressive failure stress of the coating could be reached while the stress in the graphite was kept below the tensile failure level. A second criterion of the selection was that the stiffness of the coated beam be distinctly higher than that of the uncoated beam. For a substrate thickness of 0.318 cm and an assumed coating (TiB_2) modulus of 545 GPa[7] the linear elastic modelling yielded a coating thickness of 24 μm to satisfy the first criterion and predicted the coated beam to be three times stiffer than the bare graphite.

Four point flexure testing was done on 10.2 x 1.27 x 0.318 cm beams of bare graphite and on TiB_2 and B coated beams with the coatings in both tension and compression. The tests were conducted in triplicate at room temperature, 1000, 1500 and 2000°C (1750°C for B) in an argon atmosphere. The flexure testing and the linear elastic analysis of data was performed at Southern Research Institute by B. T. Johnsen and H. S. Starrett.[8]

A factor in the relative thermal shock resistance of TiC and TiB_2 coatings is that the former may exhibit a lower temperature transition from brittle to ductile behavior. To obtain a comparison of the coating ductility of TiC and TiB_2 as a function of temperature additional tests were conducted in which coated flexure bars of similar dimensions to the above were subjected to

stress relaxation tests. Following an anneal at 1150°C for two hours, the beams were placed in a rigid four point bend fixture with the coating in compression and exposed to temperatures of 500, 850 or 1150°C for two hours in a vacuum furnace. Two beams were tested under each condition. The radius of curvature imposed on the samples was such that the coating stress at temperature would be about half the ultimate strength and the maximum tensile fiber stress on the graphite would be well below its fracture strength. After cooling to room temperature, the beams were removed from the fixture and the radius of curvature of the gage sections measured with a cathetometer. The radius of curvature, after an appropriate accounting for any permanent deformation of the graphite, (determined separately by experiment) can be related to the elastic stress in the coating and in turn the permanent strain which took place at the test temperature. The analysis utilizes the relationships developed by Brenner and Senderoff[9] for the determination of residual stress in a coating:

$$S = \frac{E_p[R(t+d)^4 - (R-1)t^4]}{6rdt(t+d)}$$

where:

$S \equiv$ stress in the coating.

$E_p \equiv$ Young's Modulus of the substrate.

$R \equiv$ ratio of Young's Modulus of coating to that of substrate.

t ≡ thickness of substrate.

d ≡ thickness of coating.

r ≡ radius of curvature.

This formula relates the uniaxial residual stress in a coating on a substrate constrained to a flat position to the radius of curvature which develops when the constraint is removed. Since the stress is proportional to the inverse radius of curvature, the formula can equally well be applied to a case of going from an initial (constrained) radius of curvature to another one (unconstrained). This is the basis for correcting for the small effect of permanent deflection of the graphite. The stress in the coating is calculated for the case of being constrained to the radius of curvature which the uncoated graphite bar assumes after its permanent deflection at the same test temperature. This stress is then converted to an elastic strain in the coating and this strain is interpreted as the permanent coating strain which takes place at the test temperature.

MATERIALS

The flexure test beams of AXF-5Q graphite were prepared for CVD coating by bead blasting with a low pressure stream of 150 μm glass beads, then ultrasonically cleaned in acetone and alcohol and vacuum baked at 200°C.

CVD coatings of TiB_2 were obtained by reacting $TiCl_4$ and B_2H_6 in a hydrogen atmosphere at 900°C in the reactor shown in Figure 1. Gas flow rates were: H_2, 900 ml/min; B_2H_6, 38.7 ml/min;

and $TiCl_4$, 0.19 ml/min. The deposition rate averaged 20 μm/hr.[10] Coatings of boron were obtained in a similar reactor by the dissociation of B_2H_6 at 550°C and a pressure of approximately 1 Torr. The diborane flow rate was 20 ml/min. and the deposition rate averaged 15 μm/hr.[11] At the completion of the coating the sample temperature was raised to 900°C for 30 min before cooling to room temperature. The TiC coating of beams for the stress relaxation tests was performed by Ultramet Corporation. The deposition was done at 30 Torr and 1300°C with equal flow rates of CH_4 and $TiCl_4$ and an excess of H_2.

Coating thickness profiles of TiB_2 on the flexure beams were obtained by the differential x-ray transmission technique and that of boron by weight gain of the sample. In all tests the coating thicknesses were verified by post-test optical fractography. A typical coating profile is shown in the post-test polished section of TiB_2 in Figure 2. The surface roughness of the graphite which results from the bead blasting is apparent and serves to emphasize that the mechanical property results must be regarded as effective properties specific to this coating structure and geometry. In addition, some surface degradation of the TiB_2 is seen.

MECHANICAL PROPERTY RESULTS

Some examples of the four point flexure curves are shown in Figure 3. At room temperature and 1000°C the test results are typified by the lower set of 20°C curves. The test with the coating in tension displays an initial slope distinctly higher than that of the bare graphite. At point A the coating fails in tension and with increased load, a lower slope is assumed corres-

ponding to that of the bare graphite. Ultimate fracture occurs at a strain usually lower (40-70%) than that of the bare graphite. When the coated sample is tested with the coating in compression the break in the slope does not occur and ultimate fracture of the sample occurs at a deflection similar to that of the bare graphite. It thus appears that the failure initiates as a tensile failure of the graphite prior to reaching the ultimate compressive strength of the coating. The stress in the coating at fracture of the graphite must therefore be regarded as a minimum bound of its compressive strength. To obtain the true compressive strength, beams with a larger coating to substrate thickness ratio would have to be tested. The upper curves of Figure 3 are typical of the 1500 and 2000°C tests. Here the difference in stiffness of coated and uncoated beams is lower (modulus ratio is smaller) and the failure of the coating does not produce as sharp a transition in slope. At 1500 and 2000°C for TiB_2 the coatings fail (in both tension and compression) prior to the ultimate failure of the graphite. For boron the same is true at 1750°C. In both tension and compression, the deflection at ultimate failure is near that of bare graphite.

The results of the flexure testing are plotted in Figures 4 and 5 with the error bars indicating the standard deviation of the three determinations. The compressive strength data represent minimum values in several cases as indicated by the arrows above the data points. The minimum compressive strengths of both TiB_2 and boron at room temperature are about five times the tensile strengths. Above 1000°C for TiB_2 and 1500°C for boron the compressive strengths

drop more drastically than do the tensile strengths. The strength and modulus values for the CVD TiB_2 coatings are found to be considerably lower than the values obtained for bulk hot pressed TiB_2 by Mandorf and Hartwig.[7] Several factors might contribute to the lower values for the coatings: The roughness of the coating surfaces and interfaces introduces a microscopic variation of coating thickness thus lowering the effective thickness of the coating. The TiB_2 appears to contain some microcracks in the as-deposited condition and also has chlorine impurity which is evolved at 1000°C and above with the possibility of some degradation of the coating. The boron is amorphous at the deposition temperature and is incompletely crystallized to the tetragonal structure in the 900°C anneal prior to testing. Further transformation to the rhombohedral structure occurs at the 1500°C test temperature and reaction with the graphite occurs at 1500 and 1750°C to form an immediate layer of B_4C.

The plastic strains occurring in the TiC and TiB_2 coatings during stress relaxation experiments are plotted vs. test temperature in Figure 6. It is seen that while all of the plastic strains are small (10^{-4} to 10^{-3}), still, they are significant with respect to the difference of thermal expansion of the coating and the AXF-5Q graphite which is on the order of 10^{-4} for a thousand degree change of temperature.[12] The TiC does exhibit substantially greater ductility at 850°C than the TiB_2. A sharp increase in the ductility of TiB_2 occurs between 850 and 1150°C and at 1150 its ductility exceeds that observed for the TiC. Other experimenters[13-15] have observed plastic flow in TiC crystals at temperatures as low as 800°C but no similar studies have been done on TiB_2.

It must be kept in mind that these tests were done in compression at stress levels which if in tension would probably exceed the tensile fracture strengths. Also, two hours was allowed for the deformation to occur whereas the time frame in thermal shock conditions is a fraction of a second. Thus the results are useful primarily to compare plastic flow propensity of the two materials.

SUMMARY

As part of a program of materials development for application to magnetic confinement fusion reactors the mechanical properties of chemical vapor deposited coatings have been studied.

Elastic moduli, tensile and compressive fracture strengths in flexure and strains to failure have been determined at temperatures up to 2000°C for 20 μm thick coatings of boron and TiB_2 on AXF-5Q graphite. The four point bend test was used and linear elastic modelling employed to extract the coating properties from the load-deflection data of the composite beams. The values of elastic moduli and fracture strengths of TiB_2 coatings were found to be lower than literature values for bulk, hot pressed TiB_2. The compressive strength values determined, however, represent a lower bound to the true value.

Comparative values of plastic flow in TiB_2 and TiC coatings on graphite have also been obtained for temperature up to 1150°C by the analysis of residual curvature of the composite beams after annealing with a fixed deflection. TiC was found to exhibit plastic flow at lower temperatures than did the TiB_2

REFERENCES

1. A. W. Mullendore, J. B. Whitley, D. M. Mattox and R. K. Thomas; Proceedings of the 8th Sym. on Engineering Problems of Fusion Research, November 13-16, 1979, San Francisco, IEEE Pub. No. 79CH1441-5 NPS Vol. III, p. 1605.

2. A. W. Mullendore, J. B. Whitley and D. M. Mattox, "The Development and Laboratory Testing of Low Z Refractory Coatings for Fusion Reactor Limiters," Presented at the 4th International Conference on Plasma Surface Interactions in Controlled Fusion Devices, April 21-25, 1980, Garmisch-Partenkirchen FRG; to be published in J. Nucl. Materials.

3. R. A. Langley, L. C. Emerson, J. B. Whitley and A. W. Mullendore, "Testing of Coated Limiters in ISX," Presented at the 4th International Conference on Plasma Surface Interactions in Controlled Fusion Devices," April 21-25, 1980, Garmisch-Partenkirchen, FRG; to be published in J. of Nucl. Materials.

4. J. B. Whitley, A. W. Mullendore, R. A. Langley, "Testing of Low-Z Coated Limiters in Tokamaks," Thin Solid Films 73 (1) 81 (1980).

5. D. M. Mattox, A. W. Mullendore, J. B. Whitley and H. O. Pierson, "Thermal Shock and Fatigue Resistant Coatings for Fusion Reactor Environments," Thin Solid Films 73 (1) 101 (1980).

6. R. J. Thomas, Sandia National Laboratories (Private Communication).

7. V. Mandorf and J. Hartwig, AIME Proc. of Conf. on High Temperature Materials II 1961, p. 455, 1963.

8. B. T. Johnsen and H. S. Starrett, Southern Research Institute Report SoRI-EAS-80-650-4371-1F.

9. Abner Brenner and Seymour Senderoff, NBS Research Paper RP1954, Vol. 42, Feb. 1949, J. of Research of the National Bureau of Standards.

10. H. O. Pierson and A. W. Mullendore, Thin Solid Films, 72 No. 3 (1980) 511-516.

11. H. O. Pierson and A. W. Mullendore, Thin Solid Films 63 (1979) 257-261.

12. A. W. Mullendore, "Characterization of Low Z Coated Materials for Fusion Reactor Applications," Sandia Laboratories Report SAND80-0809.

13. Wendell S. Williams and R. D. Schall, Journal of Applied Physics, March 1962, 33 (3) 955-962.

14. D. J. Rowcliffe and G. E. Hollox, Journal of Applied Physics, October, 1971, 6 (10), 1270-1276.

15. D. K. Chaterjee, M. G. Mendiratta and H. A. Lipsitt, Journal of Materials Science 1979, 14, 2151-2156.

FIGURE CAPTIONS

Figure 1. Chemical Vapor Deposition Apparatus.

Figure 2. Polished Section of TiB_2/Graphite Flexure Beam Tested in Compression at 1500°C.

Figure 3. Load-Deflection Curves for Typical Four Point Bend Tests of Coated Graphite.

Figure 4. Flexure Test Results for TiB_2 Coating on Graphite.

Figure 5. Flexure Test Results for Boron Coating on Graphite.

Figure 6. Calculated Plastic Strain in Coatings of Stress Relaxation Beams.

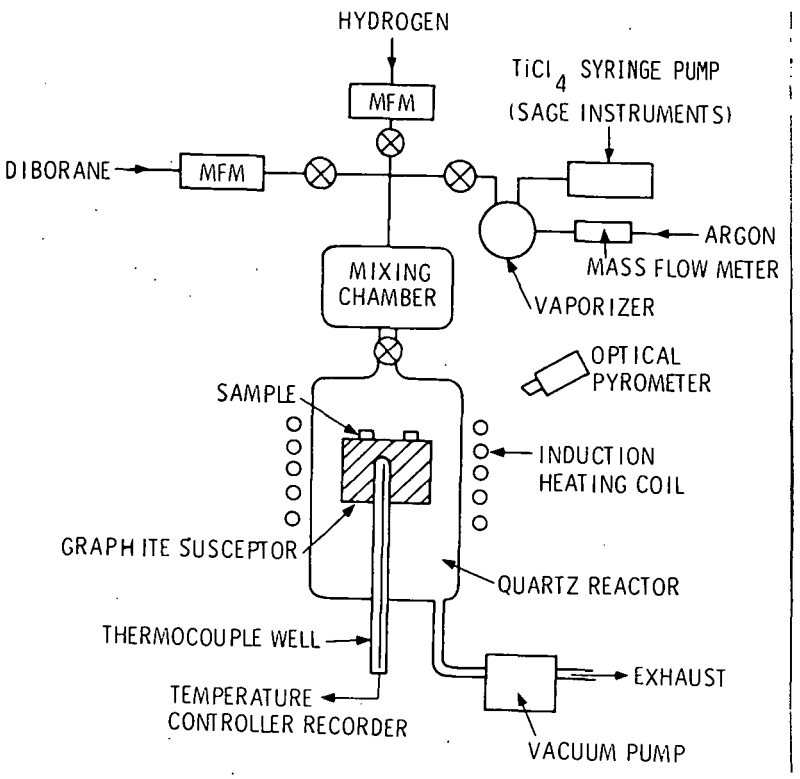

Fig. 1. Chemical Vapor Deposition Apparatus.

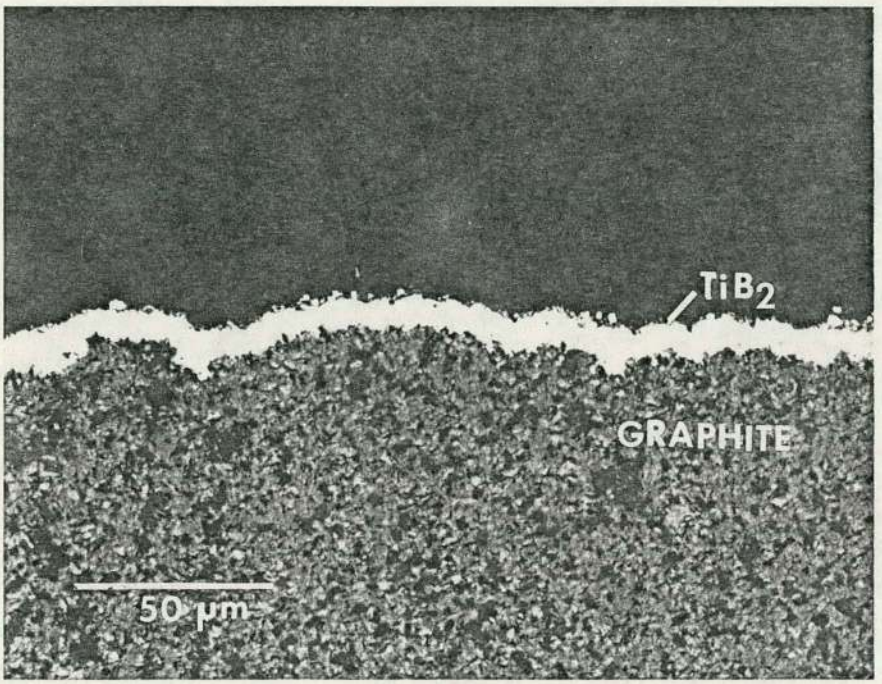

Fig. 2. Polished Section of TiB_2/Graphite Flexure Beam Tested in Compression at 1500°C.

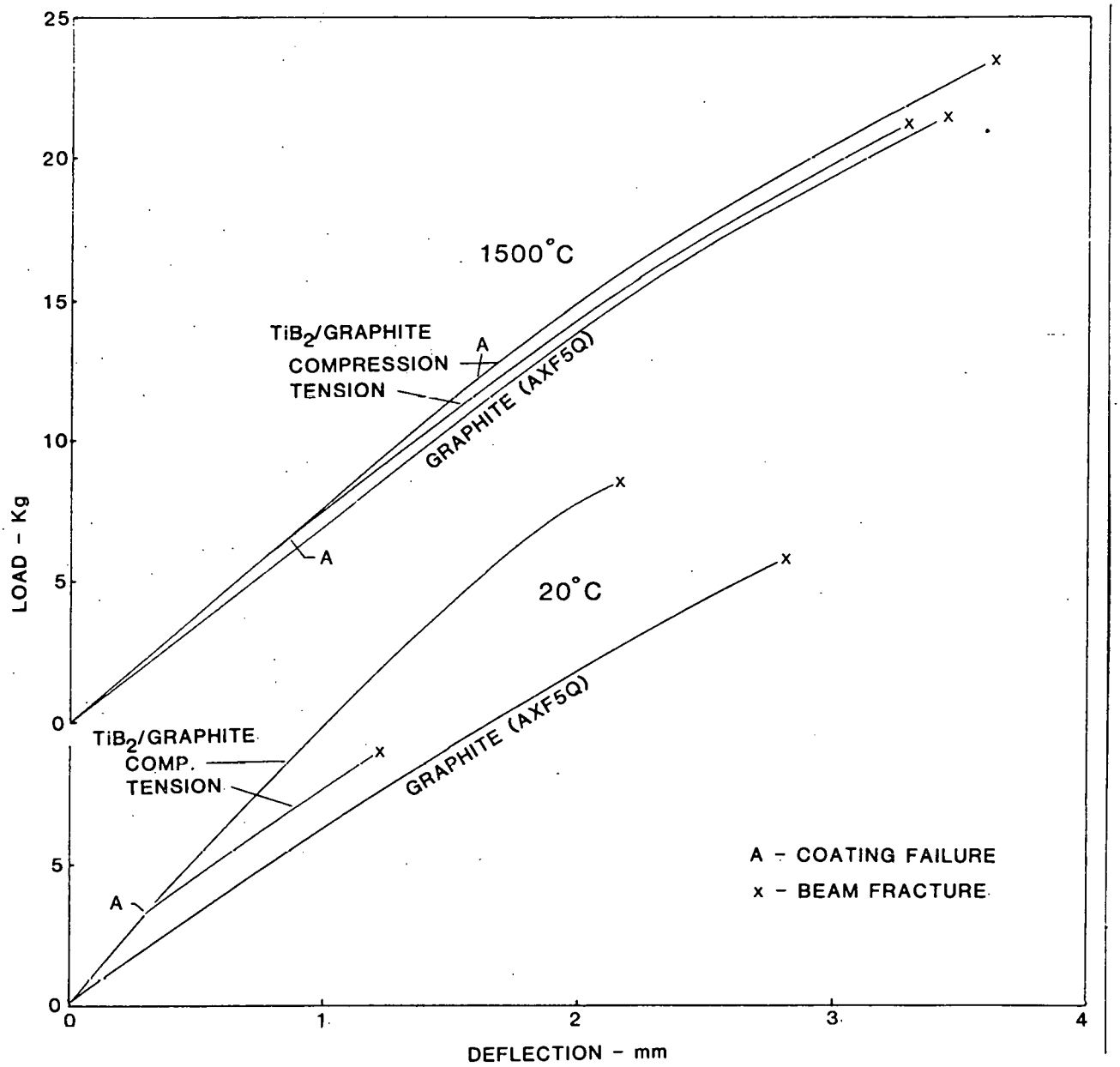

Fig. 3. Load-Deflection Curves for Typical Four Point Bend Tests of Coated Graphite.

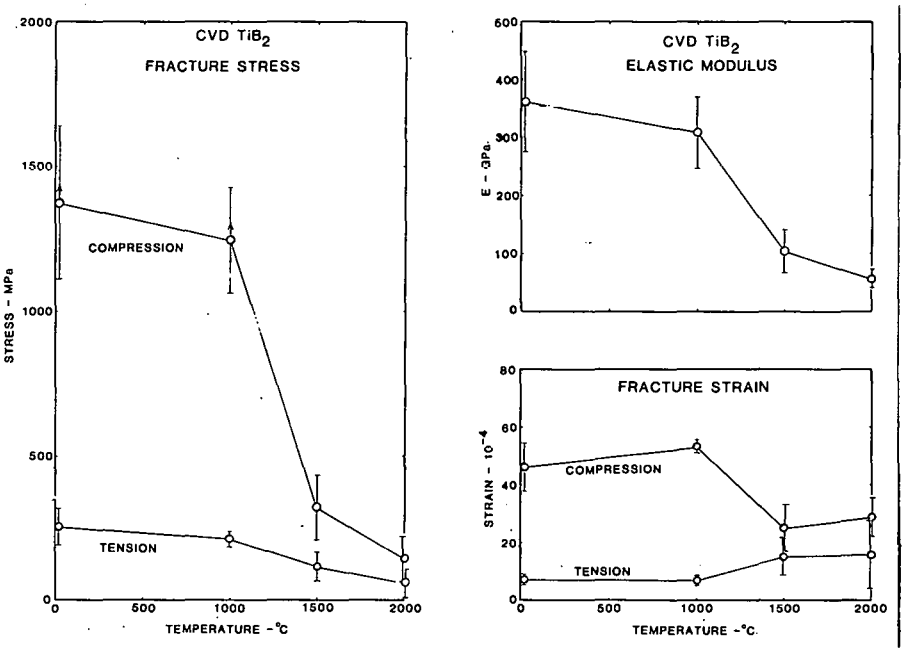

Fig. 4. Flexure Test Results for TiB_2 Coating on Graphite.

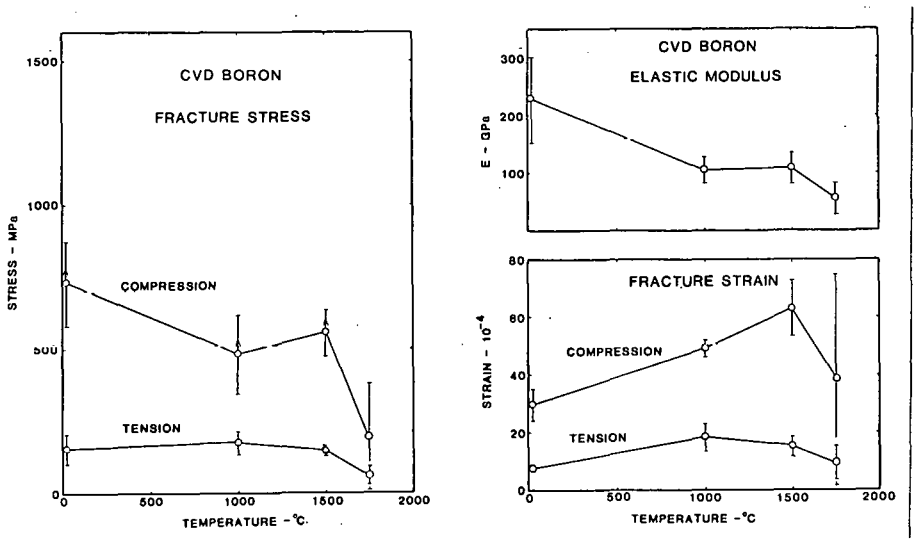

Fig. 5. Flexure Test Results for Boron Coating on Graphite.

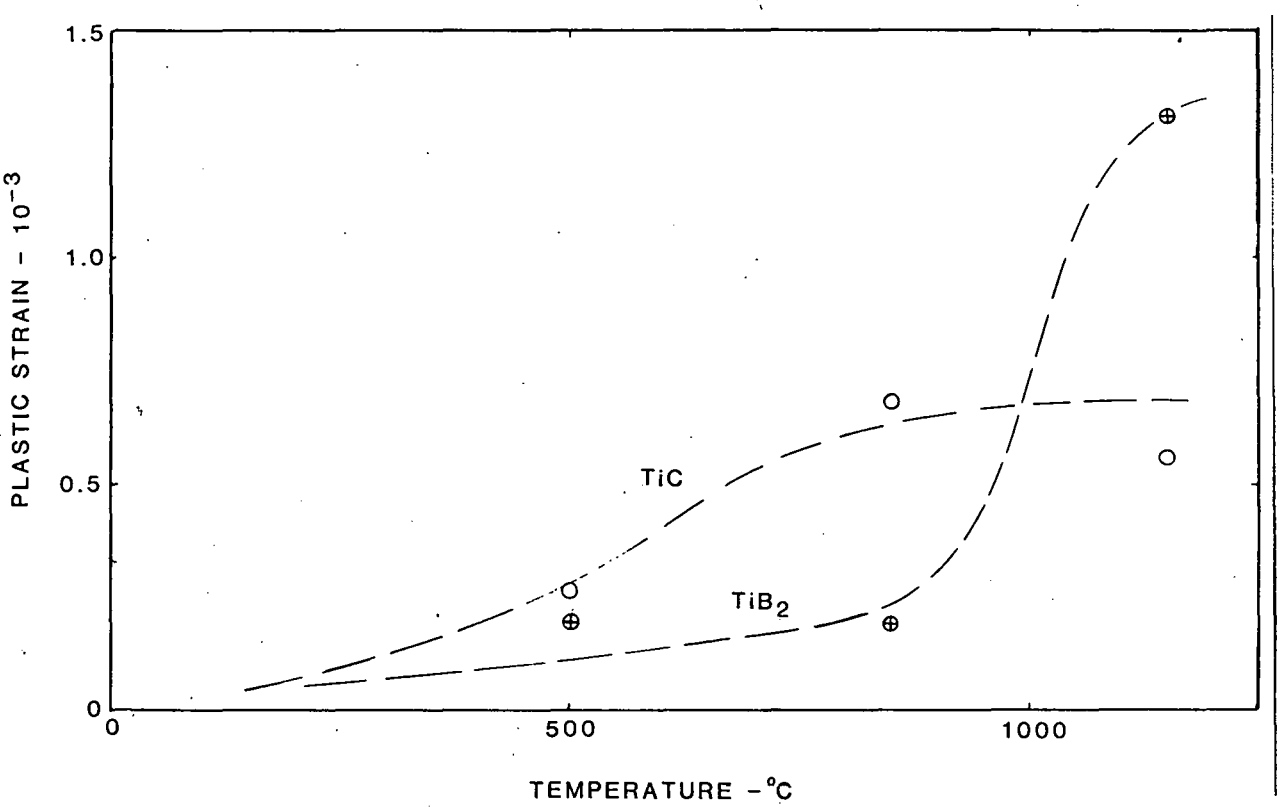

Fig. 6. Calculated Plastic Strain in Coatings of Stress Relaxation Beams.